

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
16 May 2002 (16.05.2002)

PCT

(10) International Publication Number  
**WO 02/38699 A1**

(51) International Patent Classification<sup>7</sup>: **C10G 2/00**

(21) International Application Number: **PCT/IB01/02103**

(22) International Filing Date:  
8 November 2001 (08.11.2001)

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
0027575.0 10 November 2000 (10.11.2000) **GB**

(71) Applicant (for all designated States except US): **SASOL TECHNOLOGY (PROPRIETARY) LIMITED** [ZA/ZA]; 1 Sturdee Avenue, Rosebank, 2196 Johannesburg (ZA).

(71) Applicants and

(72) Inventors: **STEYNBERG, André** [ZA/ZA]; 4 Moerdyk Street, 1911 SW5 Vanderbijlpark (ZA). **CLARKE, Simon, Charles** [GB/GB]; 65 Coalport Way, Tile Hurst, Redding, Berkshire RG30 6HY (GB).

(74) Agent: **KOTZE, Gavin, Salomon**; Adams & Adams Pretoria Office, Adams & Adams Place, 1140 Prospect Street, Hatfield, P.O. Box 1014, 0001 Pretoria (ZA).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

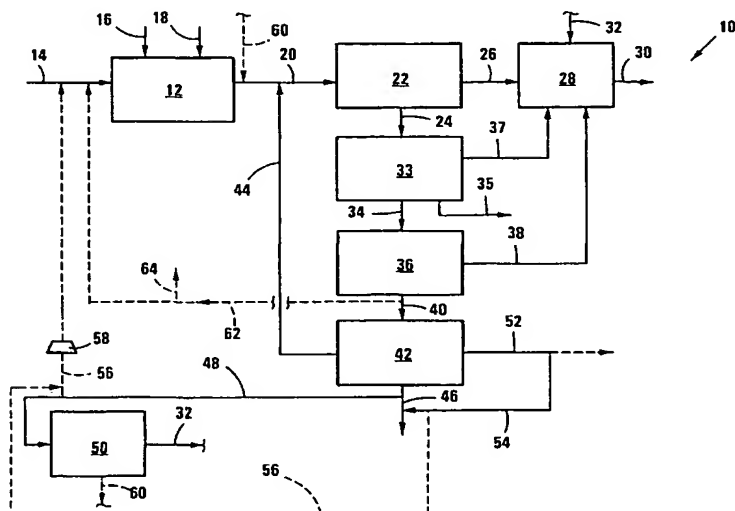
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report

[Continued on next page]

(54) Title: **PRODUCTION OF LIQUID HYDROCARBON PRODUCTS**



(57) Abstract: A process for producing liquid hydrocarbon products includes converting a natural gas feedstock to synthesis gas, which is reacted, in a hydrocarbon synthesis stage and by a Fischer-Tropsch reaction, to produce a range of hydrocarbon products. An overheads vapour phase is separated from a liquid phase, and fed to a product condensation stage, where condensation of some components thereof takes place. A vapour phase, an aqueous phase, and a condensed product phase are withdrawn. The vapour phase is fed to a vapour phase work-up stage where a gas component comprising increased concentrations of CO and H<sub>2</sub>, relative to the vapour phase feed to the vapour phase work-up stage, is recovered, with this gas component being recycled to the hydrocarbon synthesis stage.

WO 02/38699 A1



— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

5

PRODUCTION OF LIQUID HYDROCARBON PRODUCTS

10 THIS INVENTION relates to the production of liquid hydrocarbon products. It relates in particular to a process for producing liquid hydrocarbon products.

According to a first aspect of the invention, there is provided a process for producing liquid hydrocarbon products, which process includes

15 converting, in a synthesis gas production stage, a natural gas feedstock comprising mainly  $\text{CH}_4$  to synthesis gas comprising  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$ ;

feeding the synthesis gas, as a feedstock, to a hydrocarbon synthesis stage;

20 in the hydrocarbon synthesis stage, reacting the synthesis gas at elevated temperature and pressure, and in the presence of a Fischer-Tropsch catalyst, to produce a range of hydrocarbon products of differing carbon chain lengths, and separating an overheads vapour phase comprising gaseous hydrocarbon products, unreacted synthesis gas, water, and any soluble organic compounds which form in the hydrocarbon synthesis stage, from a liquid phase comprising heavier liquid hydrocarbon products;

25 withdrawing the liquid phase from the hydrocarbon synthesis stage;

30 withdrawing the overheads vapour phase from the hydrocarbon synthesis stage and feeding it to a product condensation stage, where condensation of at least some components of the overheads vapour phase takes place;

withdrawing from the product condensation stage a vapour phase comprising gaseous hydrocarbon products, an aqueous phase comprising

CONFIRMATION COPY

water and said any soluble organic compounds which form in the hydrocarbon synthesis stage, and a condensed product phase comprising condensed hydrocarbon products;

feeding the vapour phase to a vapour phase work-up stage;

5 in the vapour phase work-up stage, recovering from the vapour phase a gas component comprising increased concentrations of CO and H<sub>2</sub>, relative to the vapour phase feed to the vapour phase work-up stage; and

recycling the CO and H<sub>2</sub>-containing gas component to the hydrocarbon synthesis stage, as a feedstock component.

10

The conversion of the natural gas to synthesis gas in the synthesis gas production stage may be effected by any suitable reaction mechanism involving reacting hydrocarbonaceous material, which is primarily CH<sub>4</sub>, in the natural gas with steam and/or oxygen. Typically, the conversion may be effected by means of steam reforming, which does not require the use of oxygen; autothermal reforming, in which the hydrocarbonaceous material reacts with oxygen in a first reaction section, whereafter an endothermic steam reforming reaction takes place adiabatically in a second reaction section; ceramic oxygen transfer membrane reforming, in which oxygen required for the reforming reaction is transported through an oxygen permeable membrane into a reaction zone; plasma reforming in which the reforming reaction is driven by an electrically generated plasma; non-catalytic partial oxidation; or catalytic partial oxidation. If desired, two or more of these conversion mechanisms or technologies may be combined, eg to optimize thermal efficiency, or to obtain an optimised or beneficial synthesis gas composition.

15

20

25

30

The present invention is characterized thereby that it is not necessary to remove CO<sub>2</sub> from the synthesis gas before using it as feedstock to the hydrocarbon synthesis stage.

The hydrocarbon synthesis stage may include a suitable reactor such as a tubular fixed bed reactor, a slurry bed reactor or an ebullating bed reactor. The pressure in the reactor may be between 1 and 100 bar, while the temperature may be between 200°C and 380°C. The reactor will thus contain the Fischer-Tropsch catalyst, which will be in particulate form. The catalyst may contain, as its active catalyst component, Co, Fe, Ni, Ru, Re and/or Rh. The catalyst may be promoted with one or more promoters selected from an alkali metal, V, Cr, Pt, Pd, La, Re, Rh, Ru, Th, Mn, Cu, Mg, Zn and Zr. The catalyst may typically be a supported catalyst, in which the active catalyst component, eg Co, is supported on a suitable support. The support may be Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> or a combination of these.

In the hydrocarbon synthesis stage, the synthesis gas is thus catalytically reacted by means of so-called Fischer-Tropsch synthesis. Thus, for example, low temperature Fischer-Tropsch synthesis with a co-based catalyst may be used. The reaction temperature will then typically be in the range of 200°C to 260°C. A Co-based catalyst does not exhibit any significant water gas shift activity. Thus, in low temperature Fischer-Tropsch synthesis using a Co-based catalyst, the main reactants are H<sub>2</sub> and CO, with CO<sub>2</sub> in the synthesis gas behaving as an inert gas in the hydrocarbon synthesis stage.

The condensed product phase that is withdrawn from the product condensation stage typically comprises hydrocarbon products having 3 or more carbon atoms.

In the vapour phase work-up stage, the vapour phase may be separated into the gas component comprising the increased concentrations of CO and H<sub>2</sub> (hereinafter also referred to as the 'first gas component'), a second gas component enriched in CH<sub>4</sub>, and, optionally, a third gas component comprising mainly CO<sub>2</sub>.

In one embodiment of the invention, the third gas component may be present. The vapour phase work-up stage may then include a CO<sub>2</sub> removal step in which the third gas component is removed from the vapour phase, and a subsequent cryogenic separation step to which the residual vapour phase is subjected and in which the first gas component is cryogenically separated from the second gas component.

In another embodiment of the invention, the vapour phase work-up stage may include a heavy ends recovery step in which hydrocarbon products having 3 or more carbon atoms, and which are present in the vapour phase, are removed from the vapour phase; the residual vapour phase may then pass to a subsequent pressure swing adsorption step where it is separated into the first and second gas components, and, optionally, the third gas component. The third gas component, when present, will comprise mainly CO<sub>2</sub> and some light hydrocarbon products.

When present, the third gas component may be used as a fuel gas, for example, in the synthesis gas production stage and/or for superheating process steam and other uses.

The second gas component may be used to satisfy any remaining fuel gas demand; optionally, as a feedstock to a hydrogen production stage in which hydrogen is produced from CH<sub>4</sub>; and, optionally, in the synthesis gas production stage.

When hydrogen is produced from the second gas component, it may be added to the synthesis gas feedstock to the hydrocarbon synthesis stage, thereby to increase the synthesis gas hydrogen content. Instead, or additionally, hydrogen thus obtained may be used to upgrade the liquid hydrocarbon products produced in the hydrocarbon synthesis stage, as described in more detail hereunder.

An advantage of using the second gas component for hydrogen production, is that no treatment thereof is required for the removal of sulphur therefrom, since the second gas component is sulphur free.

5 The remainder of the second gas component, ie any residual second gas component not required for fuel gas or for hydrogen production, may be recycled as a feedstock component to the synthesis gas production stage. However, it will then be necessary to compress the gas to the same pressure as the natural gas feedstock to the synthesis gas preparation stage. Since the  
10 second gas component may still contain some CO<sub>2</sub>, CO and H<sub>2</sub>, it is less desirable for use as a feedstock component in the synthesis gas production stage.

The process may further include, in a liquid product upgrading stage,  
15 upgrading the liquid hydrocarbon products in the liquid phase withdrawn from the hydrocarbon synthesis stage as well as the hydrocarbon products in the condensed product phase from the product condensation stage. This upgrading may be effected by hydroprocessing the hydrocarbon products using hydrogen obtained from the second gas component as hereinbefore  
20 described, ie hydrogen produced in the hydrogen production stage.

According to a second aspect of the invention, there is provided a process for producing liquid hydrocarbon products, which process includes

25 converting, in a synthesis gas production stage, a natural gas feedstock comprising mainly CH<sub>4</sub> to synthesis gas comprising CO, H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>;

without removal of CO<sub>2</sub>, feeding the synthesis gas, as a feedstock, to a hydrocarbon synthesis stage;

30 in the hydrocarbon synthesis stage, reacting the synthesis gas at elevated temperature and pressure, and in the presence of a Co-based Fischer-Tropsch catalyst, to produce a range of hydrocarbon products of differing carbon chain lengths, and separating a vapour phase comprising gaseous

hydrocarbon products and unreacted synthesis gas from a liquid phase comprising heavier liquid hydrocarbon products;

withdrawing the liquid phase from the hydrocarbon synthesis stage;

withdrawing the vapour phase from the hydrocarbon synthesis stage

5 and feeding it to a heavy ends recovery stage;

in the heavy ends recovery stage, separating hydrocarbon products having 3 or more carbon atoms, from the vapour phase; and

10 recycling at least a portion of the vapour phase from the heavy ends recovery stage to the synthesis gas production stage, as a feedstock component.

In the second aspect of the invention, the synthesis gas production stage and the hydrocarbon synthesis stage may be as hereinbefore described.

15 The invention will now be described by way of example with reference to the accompanying drawings.

In the drawings,

20 FIGURE 1 shows a simplified flow diagram of a process according to one embodiment of the invention, for producing liquid hydrocarbon products; and

FIGURE 2 shows a simplified flow diagram of a process according to a second embodiment of the invention, for producing liquid hydrocarbon products.

25

Referring to Figure 1, reference numeral 10 generally indicates a process according to one embodiment of the invention, for producing liquid hydrocarbon products.

30 The process 10 includes a synthesis gas production stage 12, with a natural gas feed line 14 leading into the stage 12. An oxygen feed line 16 also leads into the stage 12, as does a steam feed line 18.



A synthesis gas line 20 leads from the stage 12 to a hydrocarbon synthesis stage 22. A liquid phase withdrawal line 26 leads from the stage 22. The liquid phase withdrawal line 26 leads into a liquid product upgrading stage 28, with an upgraded product withdrawal line 30 leading from the stage 28. A hydrogen addition line 32 leads into the stage 28.

An overheads vapour phase withdrawal line 24 leads from the stage 22 to a product condensation stage 33. An aqueous phase withdrawal line 35 leads from the stage 33, as does a condensed product phase withdrawal line 37. The line 37 leads into the product upgrading stage 28.

A vapour phase withdrawal line 34 leads from the stage 33 to a heavy ends recovery step or stage 36. A light hydrocarbon withdrawal line 38 leads from the stage 36 to the stage 28. Instead, if desired, the line 38 can lead to a separate product upgrading stage (not shown).

A vapour phase line 40 leads from the stage 36 to a pressure swing adsorption step or stage 42. A first gas component recycle line 44 leads from the stage 42 to the synthesis gas line 20.

A second gas component withdrawal line 46 leads from the stage 42. A line 48 leads from the line 46 to a hydrogen production stage 50, with the hydrogen line 32 leading from the stage 50. It will be appreciated that, if desired, the line 48 and the hydrogen production stage can be dispensed with.

A third gas component withdrawal line 52 leads from the stage 42, with a line 54 connecting the line 52 to the line 46, so that the third gas component produced in the stage 42 can also be used as fuel gas, as hereinafter described.

In use, natural gas is introduced along the line 14 into the synthesis gas production stage 12. Typically, the stage 12 is provided by an autothermal reformer in which hydrocarbonaceous material, mainly methane, present in the natural gas reacts with oxygen which enters the reformer through the line 16, in a first section of the reformer. Thereafter, endothermic steam reforming, using steam which enters along the line 18, occurs adiabatically in a second section of the reformer. The autothermal reformer typically uses a low steam to carbon ratio of about 0.2:1 to about 0.6:1, with the outlet gas temperature being from 1000°C to 1100°C.

Synthesis gas comprising CO, H<sub>2</sub>, CO<sub>2</sub> and some residual methane passes from the stage 12 along the flow line 20 to the hydrocarbon synthesis stage 22. There is no removal of CO from the synthesis gas between the stages 12, 22. In the stage 22, H<sub>2</sub> and CO in the synthesis gas are reacted, at a temperature of 200°C to 280°C, a pressure of between 1 and 100 bar, typically about 25 bar, and in the presence of a cobalt-based catalyst, using so-called low temperature Fischer-Tropsch synthesis, to produce a range of hydrocarbon products of differing carbon chain lengths. The products are separated into a liquid phase comprising heavier liquid hydrocarbons, and an overheads vapour phase comprising light hydrocarbon products, unreacted synthesis gas, water and soluble organic compounds such as alcohols. The liquid phase is withdrawn along the line 26 to the product upgrading stage 28 where the liquid hydrocarbon products are upgraded by means of hydroprocessing into more valuable products, which are withdrawn along the line 30.

The overheads vapour phase is withdrawn along the line 24 and passes into the product condensation unit 33. An aqueous phase comprising water and any soluble organic compounds is withdrawn along the line 35. A condensed product phase, typically comprising hydrocarbon products having 3 or more carbon atoms, is withdrawn along the line 37 and passes into the product upgrading stage 28.

A vapour phase is withdrawn along the line 34 and passes to the heavy ends recovery stage 36 where light hydrocarbon products having carbon numbers of 3 or more, ie having 3 or more carbon atoms, are separated out and withdrawn along the line 38. The residual vapour phase passes along the line 40 to the pressure swing adsorption stage 42 where it is separated into a first gas component comprising mainly CO and H<sub>2</sub>, a second gas component enriched in CH<sub>4</sub>, and a third gas component comprising mainly CO<sub>2</sub>. The first gas component is recycled, along the line 44, to the synthesis gas line 20.

The heavy ends recovery in the stage 36 may be provided by an oil absorber (typically using chilled oil) or by cooling the vapour phase to temperatures close to (but slightly above) the CO<sub>2</sub> solidification temperature. Use may also be made of temperature swing adsorption.

The second gas component is withdrawn along the line 46, and a portion thereof is used as fuel gas. A portion of the second gas component passes along the flow line 48 to the hydrogen production stage 50 where hydrogen is produced. The hydrogen is withdrawn along the line 32 and is used for upgrading the liquid products in the stage 28.

The third gas component is withdrawn along the line 52 and is routed, by means of the line 54, to the line 46 so that it is also used as fuel gas. In another version (not shown) of this embodiment of the invention, no third gas component is produced in the stage 42. The lines 52, 54 are then dispensed with.

If there is an excess of second gas component over and above that required as fuel gas and for hydrogen production, it can be recycled, along a flow line 56, to the natural gas flow line 14 to the synthesis gas production stage 12. Thus, it is then used as a feedstock component. However, it then requires compression in a compressor 58. Additionally, it may contain some CO<sub>2</sub>, CO

and  $H_2$  so that it is less desirable to use the second gas component as a feedstock component to the synthesis gas production stage 12.

If desired, hydrogen produced in the stage 50 can be routed, along a flow line 60, to the synthesis gas flow line 20 leading to the hydrocarbon synthesis stage 22. In this fashion, the  $H_2:CO$  ratio in the synthesis gas feed to the stage 22 can be adjusted, if necessary, eg depending on the efficiency of the various separations and the reformer operating conditions in the stage 12.

In another version of the invention, instead of having the pressure swing adsorption stage 42 and the hydrogen production stage 50, the vapour phase from the heavy ends recovery stage 36 can be recycled to the synthesis gas preparation stage 12, by means of a recycle line 62, so that the vapour phase is used as a feedstock component. Some of the vapour phase can then be withdrawn, along a flow line 64, for use as fuel gas in the stages 12, 22.

If desired, a portion (not shown) of the vapour phase or tail gas from the hydrocarbon synthesis stage 22 can then be recycled, upstream of the heavy ends recovery stage 36, to the stage 22.

In the heavy ends recovery stage 36, any suitable physical separation method may be used. However, preferably, the removal of the light hydrocarbon products may involve cooling the vapour stream, at elevated pressure, to a temperature above the  $CO_2$  solidification temperature at that pressure, and then separating a condensed liquid phase from an uncondensed vapour phase. The cooling can be performed by using, for example, a refrigeration cycle employing a suitable refrigerant. Alternatively, a turbo expander is used to provide a significant portion of the cooling duty. Temperature swing adsorption and oil adsorption are alternatives to cooling and condensation as hereinbefore described.

Referring to Figure 2, reference numeral 100 generally indicates a process according to a second embodiment of the invention, for producing liquid hydrocarbon products.

5 In the process 100, components which are the same or similar to those of the process 10 hereinbefore described with reference to Figure 1, are indicated with the same reference numerals.

10 In the process 100, the heavy ends recovery stage 36 and the pressure swing adsorption stage 42 are dispensed with. Instead, a CO<sub>2</sub> removal step or stage 102 and a cryogenic separation step or stage 104 are provided.

15 Thus, the vapour phase flow line 34 from the product condensation stage 33 leads into the CO<sub>2</sub> removal stage 102. The third gas component withdrawal line 52 leads from the CO<sub>2</sub> removal stage 102 and is vented to the atmosphere.

20 A vapour phase transfer line 106 leads from the stage 102 to the cryogenic separation stage 104, with the first gas component line 44 and the second gas component line 46 leading from the stage 104.

25 It is believed that, in the process 100, efficient separations of the first, second and third gas components from one another can be achieved; however, it is also believed that capital costs and energy requirements may be higher than in the case of the process 10.

30 The Applicant is aware of processes for producing liquid hydrocarbon products and which include reforming a gaseous feedstock to synthesis gas in a reformer, reacting the synthesis gas in a Fischer-Tropsch synthesis stage, and separating an overheads vapour phase from a liquid hydrocarbon product phase. The overheads vapour phase is separated into tail gas, water and

hydrocarbon products. The tail gas is split, with a portion being recycled to the feedstock to the reformer, while the remainder is used as fuel gas.

However, such known processes have disadvantages such as

- 5 • residual tail gas from the Fischer-Tropsch synthesis stage, after optimization of vapour phase or tail gas recycle to the reformer, is often in excess of the fuel requirements;
- valuable  $H_2$  and CO components in the tail gas are partially destroyed by recycling them to the reformer or completely destroyed by burning them in  
10 the fuel gas;
- tail gas recycle causes the build-up of inerts, which decreases the partial pressure of the reactants, ie  $H_2$  and CO.

These disadvantages are avoided or overcome in the process of the present  
15 invention. For example, valuable  $H_2$  and CO components in the tail gas are not destroyed, but are recycled to the Fischer-Tropsch synthesis stage. Furthermore, cost savings are realized in the process of the invention, and in particular in the Fischer-Tropsch synthesis stage 22, since it is possible to achieve, in the processes 10, 100, conversions which are equal to or better  
20 than those obtained in the known processes in respect of CO and  $H_2$  to raw liquid products, using fewer or smaller Fischer-Tropsch reactors. Additionally, the ratio of raw liquid products to natural gas feed is increased. Still further, the cost of synthesis gas preparation per unit of reactants ( $CO + H_2$ ) produced, is decreased. As a result, the economics of the processes 10, 100  
25 are significantly improved as compared to the known processes.

Still further, in the case of autothermal reforming, recycle of  $CO_2$  to the reformer can be avoided by decreasing the steam to reformable carbon ('s/c') ratio, typically to values between 0.2 and 0.6, depending on the natural gas  
30 composition. This can also be achieved using partial oxidation, but, as is required in known processes, oxygen consumption is higher due to the higher outlet temperatures, and additional  $H_2$  recycle may then be needed to increase

the H<sub>2</sub>/CO ratio. The disadvantage of lower s/c ratios is that the methane conversion decreases unless the outlet temperature of the reformer is increased above the typically recommended temperature of 900°C to 1050°C. Increasing the outlet temperature is undesirable, since this consumes more oxygen. A further disadvantage of using lower s/c ratios without the present invention or high reformer outlet temperatures, is that if the tail gas from the hydrocarbon synthesis section is all routed to fuel gas, the tail gas availability then exceeds the fuel gas demand. Since plants for producing liquid hydrocarbons are often located in remote areas, there are usually no, or limited, alternative uses for the tail gas such as for generating electricity. It is due to these effects that the optimum reformer steam-to-carbon ratio in the known processes is generally higher than in the processes 10, 100, eg typically at about 0.6:1.

The invention thus provides a thermally efficient integrated process for the production of liquid hydrocarbons.

CLAIMS

1. A process for producing liquid hydrocarbon products, which  
5 process includes

converting, in a synthesis gas production stage, a natural gas feedstock comprising mainly  $\text{CH}_4$  to synthesis gas comprising  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$ ;

feeding the synthesis gas, as a feedstock, to a hydrocarbon synthesis stage;

10 in the hydrocarbon synthesis stage, reacting the synthesis gas at elevated temperature and pressure, and in the presence of a Fischer-Tropsch catalyst, to produce a range of hydrocarbon products of differing carbon chain lengths, and separating an overheads vapour phase comprising gaseous hydrocarbon products, unreacted synthesis gas, water, and any soluble  
15 organic compounds which form in the hydrocarbon synthesis stage, from a liquid phase comprising heavier liquid hydrocarbon products;

withdrawing the liquid phase from the hydrocarbon synthesis stage;

withdrawing the overheads vapour phase from the hydrocarbon synthesis stage and feeding it to a product condensation stage, where  
20 condensation of at least some components of the overheads vapour phase takes place;

withdrawing from the product condensation stage a vapour phase comprising gaseous hydrocarbon products, an aqueous phase comprising water and said any soluble organic compounds which form in the hydrocarbon  
25 synthesis stage, and a condensed product phase comprising condensed hydrocarbon products;

feeding the vapour phase to a vapour phase work-up stage;

in the vapour phase work-up stage, recovering from the vapour phase a gas component comprising increased concentrations of  $\text{CO}$  and  $\text{H}_2$ , relative to  
30 the vapour phase feed to the vapour phase work-up stage; and

recycling the  $\text{CO}$  and  $\text{H}_2$ -containing gas component to the hydrocarbon synthesis stage, as a feedstock component.



2. A process according to Claim 1, wherein the conversion of the natural gas to synthesis gas in the synthesis gas production stage is effected by a reaction mechanism involving reacting hydrocarbonaceous material with steam and/or oxygen, with the reaction mechanism being selected from the group consisting in steam reforming, which does not require the use of oxygen; autothermal reforming, in which the hydrocarbonaceous material reacts with oxygen in a first reaction section, whereafter an endothermic steam reforming reaction takes place adiabatically in a second reaction section; ceramic oxygen transfer membrane reforming, in which oxygen required for the reforming reaction is transported through an oxygen permeable membrane into a reaction zone; plasma reforming in which the reforming reaction is driven by an electrically generated plasma; non-catalytic partial oxidation; catalytic partial oxidation; and two or more of these reaction mechanisms.

3. A process according to Claim 1 or Claim 2, wherein no CO<sub>2</sub> removal from the synthesis gas is effected, prior to the synthesis gas being fed as the feedstock to the hydrocarbon synthesis stage.

4. A process according to any one of Claims 1 to 3 inclusive, wherein the hydrocarbon synthesis stage includes a reactor in which the synthesis gas is catalytically reacted by means of low temperature Fischer-Tropsch synthesis using a Co-based Fischer-Tropsch catalyst, with the reaction temperature being in the range of 200°C to 280°C, with the main reactants being H<sub>2</sub> and CO, and with the CO<sub>2</sub> in the synthesis gas behaving as an inert gas in the reactor.

5. A process according to Claim 4 wherein, in the vapour phase work-up stage, the vapour phase is separated into the gas component comprising the increased concentrations of CO and H<sub>2</sub> (the 'first gas

component'), a second gas component enriched in  $\text{CH}_4$ , and, optionally, a third gas component comprising mainly  $\text{CO}_2$ .

6. A process according to Claim 5, wherein the third gas component is present, with the vapour phase work-up stage including a  $\text{CO}_2$  removal step in which the third gas component is removed from the vapour phase, and a subsequent cryogenic separation step to which the residual vapour phase is subjected and in which the first gas component is cryogenically separated from the second gas component.

7. A process according to Claim 5, wherein the third gas component is present, with the vapour phase work-up stage including a heavy ends recovery step in which hydrocarbon products having 3 or more carbon atoms, and which are present in the vapour phase, are removed from the vapour phase, and with the residual vapour phase then passing to a subsequent pressure swing adsorption step where it is separated into the first, second and third gas components, with the third gas component thus comprising mainly  $\text{CO}_2$  and some light hydrocarbon products.

8. A process according to Claim 7, wherein the second gas component is fed into a hydrogen production stage in which hydrogen is produced from the  $\text{CH}_4$ .

9. A process according to Claim 8, wherein hydrogen produced in the hydrogen production stage is added to the synthesis gas feedstock to the hydrocarbon synthesis stage, thereby to increase the synthesis gas hydrogen content.

10. A process according to Claim 7 or Claim 8, which includes, in a liquid product upgrading stage, upgrading the liquid hydrocarbon products in the liquid phase withdrawn from the hydrocarbon synthesis stage as well as the hydrocarbon products in the condensed product phase from the product

condensation stage, by hydroprocessing the hydrocarbon products using hydrogen from the hydrogen production stage.

11. A process for producing liquid hydrocarbon products, which process includes

converting, in a synthesis gas production stage, a natural gas feedstock comprising mainly  $\text{CH}_4$  to synthesis gas comprising  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$ ;

without removal of  $\text{CO}_2$ , feeding the synthesis gas, as a feedstock, to a hydrocarbon synthesis stage;

in the hydrocarbon synthesis stage, reacting the synthesis gas at elevated temperature and pressure, and in the presence of a Co-based Fischer-Tropsch catalyst, to produce a range of hydrocarbon products of differing carbon chain lengths, and separating a vapour phase comprising gaseous hydrocarbon products and unreacted synthesis gas from a liquid phase comprising heavier liquid hydrocarbon products;

withdrawing the liquid phase from the hydrocarbon synthesis stage;

withdrawing the vapour phase from the hydrocarbon synthesis stage and feeding it to a heavy ends recovery stage;

in the heavy ends recovery stage, separating hydrocarbon products having 3 or more carbon atoms, from the vapour phase; and

recycling at least a portion of the vapour phase from the heavy ends recovery stage to the synthesis gas production stage, as a feedstock component.

12. A process according to Claim 11, wherein the conversion of the natural gas to synthesis gas in the synthesis gas production stage is effected by a reaction mechanism involving reacting hydrocarbonaceous material with steam and/or oxygen, with the reaction mechanism being selected from the group consisting in steam reforming, which does not require the use of oxygen; autothermal reforming, in which the hydrocarbonaceous material reacts with oxygen in a first reaction section, whereafter an endothermic steam reforming reaction takes place adiabatically in a second reaction

section; ceramic oxygen transfer membrane reforming, in which oxygen required for the reforming reaction is transported through an oxygen permeable membrane into a reaction zone; plasma reforming in which the reforming reaction is driven by an electrically generated plasma; non-catalytic partial oxidation; catalytic partial oxidation; and two or more of these reaction mechanisms.

13. A process according to Claim 11 or Claim 12, wherein the hydrocarbon synthesis stage includes a reactor in which the synthesis gas is catalytically reacted by means of low temperature Fischer-Tropsch synthesis using the Co-based Fischer-Tropsch catalyst, with the reaction temperature being in the range of 200°C to 280°C, with the main reactants being H<sub>2</sub> and CO, and with the CO<sub>2</sub> in the synthesis gas behaving as an inert gas in the reactor.

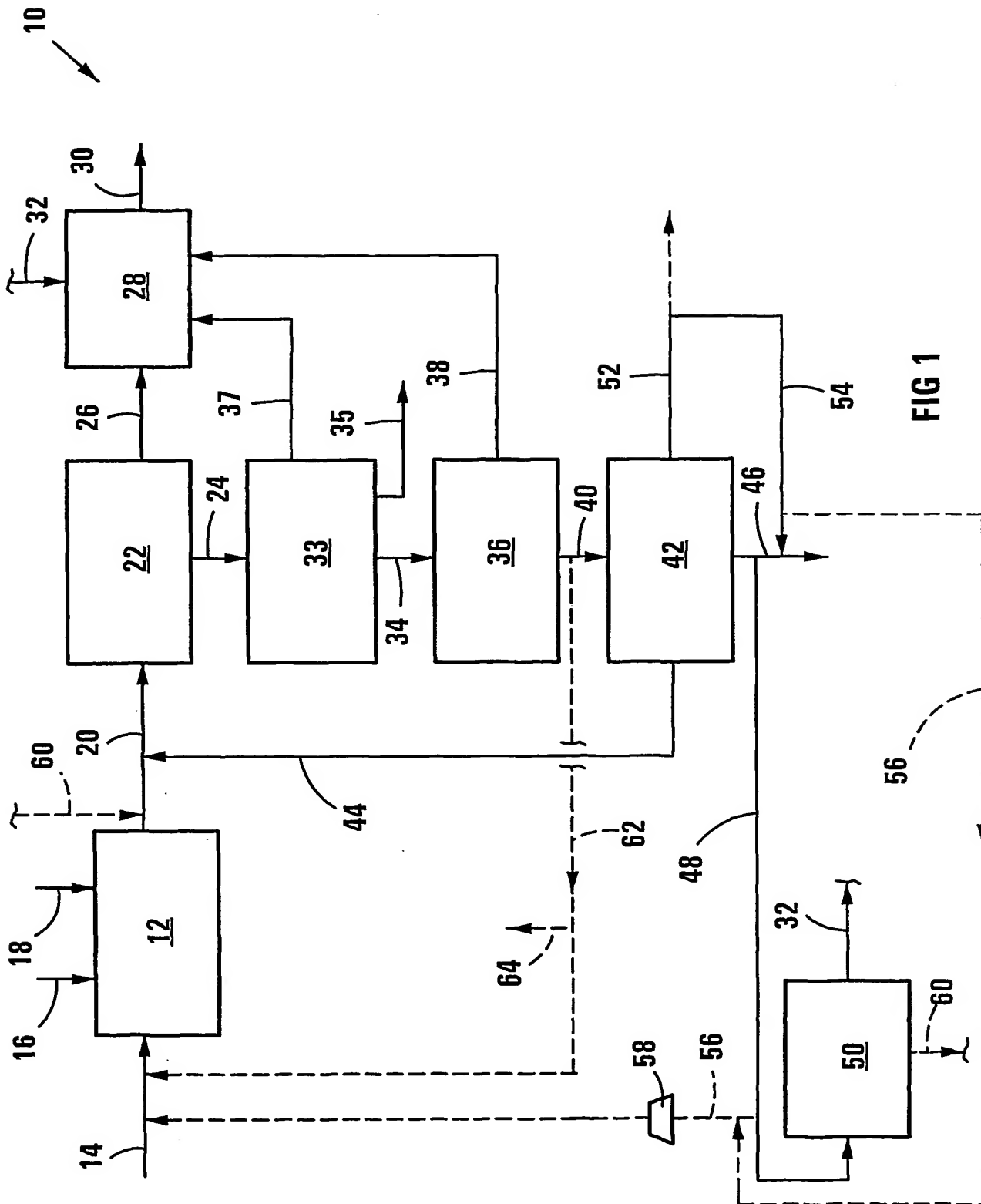
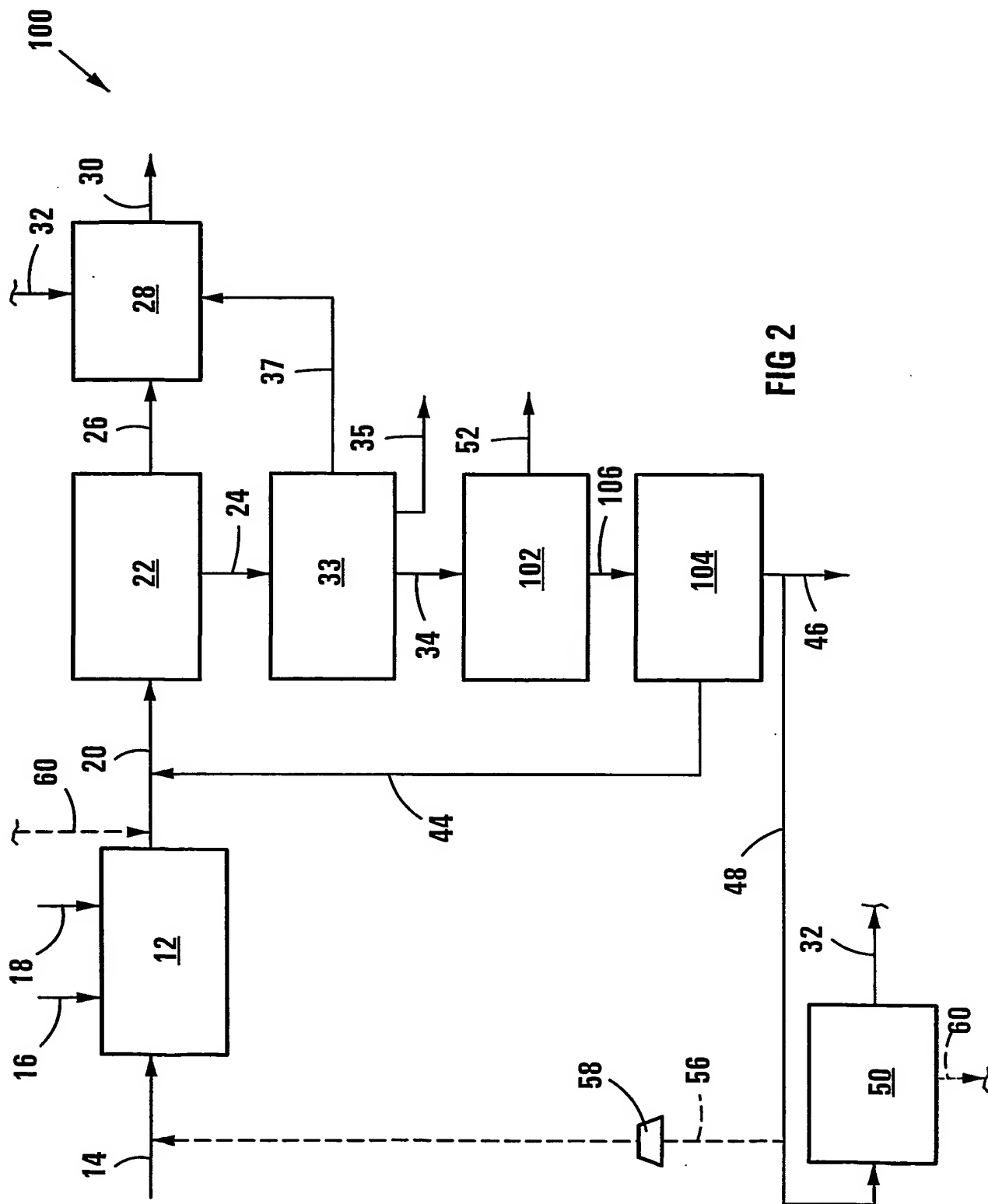


FIG 1



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 01/02103

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G2/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 587 008 A (MINDERHOUD JOHANNES K ET AL) 6 May 1986 (1986-05-06) claims 1,3,7,8,10,11 ---	1,2,4,7, 10-13
A	EP 0 516 441 A (BRITISH PETROLEUM CO PLC) 2 December 1992 (1992-12-02) claims 1,3,4 figures 1-5 ---	1-4,9, 11-13
A	GB 780 577 A (RURRCHEMIE AG;LURGI GES FUER WAERMETECHNIK M) 7 August 1957 (1957-08-07) claims 1-9 page 2, line 6 - line 15 page 2, line 28 - line 31 ---	1-4, 11-13
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

15 March 2002

Date of mailing of the international search report

25/03/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

De Herdt, 0

## INTERNATIONAL SEARCH REPORT

Inter al Application No  
PCT/IB 01/02103

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 223 029 A (SHELL INT RESEARCH) 28 March 1990 (1990-03-28) claims 1,3 page 3, line 30 -page 4, line 10 -----	1-4, 11-13
A	GB 1 439 769 A (SOUTH AFRICAN COAL OIL GAS) 16 June 1976 (1976-06-16) claim 1 example 5 -----	1,6
A	GB 2 246 576 A (SHELL INT RESEARCH) 5 February 1992 (1992-02-05) claim 1 page 5, line 13 - line 32 page 6, line 6 - line 15 -----	1-4



## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 01/02103

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4587008	A	06-05-1986	AT 42946 T	15-05-1989
			AU 565645 B2	24-09-1987
			AU 3538184 A	23-05-1985
			BR 8405783 A	17-09-1985
			CA 1234158 A1	15-03-1988
			DE 3478108 D1	15-06-1989
			EP 0142888 A2	29-05-1985
			ES 537607 D0	16-10-1985
			ES 8601079 A1	16-02-1986
			GB 2149813 A , B	19-06-1985
			IN 162399 A1	21-05-1988
			JP 60124694 A	03-07-1985
			NZ 210203 A	30-09-1987
			US 4628133 A	09-12-1986
			ZA 8408827 A	26-06-1985
EP 0516441	A	02-12-1992	AT 165073 T	15-05-1998
			AU 663082 B2	28-09-1995
			AU 1717292 A	03-12-1992
			CA 2068115 A1	01-12-1992
			CN 1067067 A , B	16-12-1992
			DE 69225089 D1	20-05-1998
			DE 69225089 T2	06-08-1998
			EP 0516441 A1	02-12-1992
			FI 922352 A	01-12-1992
			JP 6184559 A	05-07-1994
			MX 9202577 A1	01-01-1993
			NO 922120 A	01-12-1992
			NZ 242569 A	26-07-1994
			ZA 9203385 A	27-01-1993
GB 780577	A	07-08-1957	NONE	
GB 2223029	A	28-03-1990	NONE	
GB 1439769	A	16-06-1976	ZA 7206057 A	29-05-1974
			BE 804406 A1	02-01-1974
			DE 2343032 A1	04-04-1974
			FR 2197843 A1	29-03-1974
			JP 49062402 A	17-06-1974
			NL 7311736 A	07-03-1974
GB 2246576	A	05-02-1992	NONE	

**This Page Blank (uspto)**